Ion-Exchange Equilibrium Between Micro-Inhomogeneous Solid Polyelectrolyte and Aqueous Salt Solution

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Phase equilibria of aqueous solution with polyelectrolyte membranes play an important role in technological and biological separation processes. They are involved in living cell metabolism and widely used in chemical sensors, fuel cells, and electrochemical synthesis. Nevertheless, the thermodynamic and structural behavior of polymeric membranes and their equilibrium with liquid solution is not properly understood.

The present study is focused on perflourosulfonated membranes, an example of hydrophobic polymer electrolytes having microscopically inhomogeneous domains. The experimental data on membrane swelling and ion-exchange equilibrium are obtained for H+, Li+, K+, Ca_2+, Mg_2+, Fe_3+. When brought to equilibrium with aqueous salt solution the membrane reveals structural changes with solution composition, and significant hysteresis is observed in the macroscopic property – composition curves. A thermodynamic model is proposed to describe the distribution of components between liquid solution and the solid swollen membrane. Free energy contributions related to the formation of solution-filled micro-cavities in the membrane interior are estimated. The Helfrich-Safran expressions for the work of deformation of a curved interface are used to describe cavities of different shape. The predominance of cavities having specific shape (spheres, cylinders) results in a specific shift of the Donnan equilibrium, which thus becomes dependent on the microstructure of the membrane.

Different types of predicted thermodynamic behavior of a membrane in a liquid solution, including the hysteresis curves, are discussed. The results of model calculations are compared with our experimental data on the distribution of ions between the aqueous solution and the membrane. The model takes into account the effect of micro-inhomogeneties, and helps establishing the link between molecular characteristics of the perfluoropolymer membrane and its macroscopic behavior in liquid solution.